TRENDS IN THE EVOLUTION OF FLY ASH SIZE DURING COMBUSTION

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ABSTRACT

Processes governing the evolution of the intermediate ash (inorganic gases, liquids, and solids) during pulverized coal combustion were examined in detail by combusting carefully sized fractions of Beulah lignite and Upper Freeport bituminous coals in a laminar flow drop-tube furnace. Char (partially combusted coal) and fly ash produced at various temperatures and residence times were analyzed using advanced scanning electron microprobe techniques. Fly ash was collected and sized in multicyclone and impactor devices. Work was focused on determining the relationship between the sizes of the original coal and coal minerals and the size of the resulting fly ash. Time-resolved size distributions of inorganic phases associated with chars show that Beulah and Upper Freeport phases exhibit some coalescence of inorganic phases with time. The Upper Freeport shows an initial increase in the amount of particles in the lower size ranges possibly due to fragmentation of minerals or the formation of smaller inorganic ash droplets from submicron minerals or organically associated inorganic constituents. The level of ash and coal minerals in size ranges greater than 3 microns is nearly equal for Upper Freeport, possibly indicating the influence of fragmentation. Size distributions of both the Upper Freeport coal minerals and resulting fly ash were larger than similar distributions for the Beulah. Both coals gave slightly smaller fly ash sizes for higher gas temperatures. In support of this observation, calculations revealed that both coals produced more fly ash particles per coal particle for higher combustion temperatures. The mechanism of fly ash formation for the Beulah was the result of partial coalescence of minerals and organically bound constituents. Upper Freeport ash revealed coalescence for the smaller (<3.0 μm) minerals. Using different coal sized fractions and the same gas temperature of 1500°C, larger fly ash particle size distributions were observed for the smaller-sized coal fractions.

INTRODUCTION

Today's coal energy technologies are being severely challenged by tighter pollution control regulations and demands to obtain higher yields from lower quality coals. Research on the chemical and physical transformations of inorganic components during combustion is a relevant branch of coal energy research geared to meet the challenge of today's demands because the results obtained pertain not only to emissions, but also to boiler efficiency. Intermediate inorganic components in combustion systems consist of inorganic gas, liquid, and solid phases produced during the combustion of coal. These inorganic components can cause significant problems in utility boilers, including:

fireside ash deposition on heat transfer surfaces, erosion and corrosion of boiler parts, and production of fly ash that is difficult to collect. The goal is to develop a means to predict the particle-size distribution and chemistry of the fly ash for a given coal, based on the character of the initial coal inorganic constituents and combustion conditions. In order to attain this goal, quantitative data is needed to describe the transformation of coal inorganic components to fly ash particulate, so that realistic predictive models can be devised. Carefully controlled laboratory-scale combustion regimes are being used, such as the laminar flow drop-tube furnace, which can simulate gas temperatures, particle residence times, and particulate stream flow rates in larger scale combustors. Also, more sophisticated analytical tools are now available which provide a more comprehensive means of quantifying inorganic constituents in coals, fly ash, and ash deposits (1,2).

Studies of fly ash particle sizes indicate a bimodal size distribution (3,4,5,6). The submicron size particles have an average diameter of about 0.1 micrometer. These small particles form as a result of the homogeneous condensation of flame-volatilized species. Flame-volatilized species may also condense heterogeneously on the surfaces of larger particles. Larger-sized particles are sometimes referred to as residual ash, which is largely derived from discrete mineral grains. The composition and size distribution of the larger particles are a result of the transformations and interactions between discrete mineral grains and organically bound inorganic components in the coal. Processes such as coalescence, fragmentation of minerals and char, and shedding of inorganic components all play a role in the final fly ash produced. Loehden et al., (7) indicate that three potential models for fly ash generation can be used to describe fly ash particle size and composition evolution. The first, "fine limit," assumes that each mineral grain forms a fly ash particle and that the organically associated elements form fly ash particles less than 2 μm. The second, total coalescence assumes one fly ash particle forms per coal particle. The third limit, partial coalescence, suggests that the fly ash composition and particle size evolves due to partial coalescence.

The focus of work presented in this paper was to observe trends of fly ash particle size evolution during combustion of low-rank Beulah lignite and higher-rank Upper Freeport bituminous coals. The approach was to carefully quantify the association and size of the inorganic constituents in the original coal and examine the combustion products quenched at successively longer residence times in an entrained laminar flow drop-tube furnace. In this way the stages of fly ash development can be discerned for coals of varying rank and composition. Accurate information of how ash particle sizes and compositions change with time and how specific coal inorganics and minerals are transformed and other new high-temperature products formed may lead to recognizing trends in fly ash evolution.

EXPERIMENTAL

Coal and Char Characterization

Sonically sieved fractions of Beulah and Upper Freeport coals (38-53-μm, 53-74-μm, and 74-106-μm fractions) were prepared. Extensive testing of these coal fractions and their combustion by-products were performed as part of a Department of Energy contract to study inorganic transformations during combustion. Computer-controlled scanning electron microscopy (CCSEM) (1,2) was

used to ascertain abundance and size distribution of minerals or inorganic phases in the coals and chars. Standard ash determination and bulk coal ash analyses were also performed on the coal fractions. Chemical fractionation analysis (8) of the Beulah lignite gave 92% of the sodium and 46% of the calcium as being organically bound in the coal matrix. Table 1 summarizes the initial coal characterization data for Beulah and Upper Freeport.

Production and Characterization of Ash Constituents

Time-resolved studies of the evolution of fly ash particle size were accomplished for the Beulah and Upper Freeport coals by tracking particle-size transformations beginning with the original coal minerals, progressing through short residence time chars, and ending in the near 100% carbon burnout. Fly ash and char were produced using an entrained flow-tube furnace, also known as a drop-tube furnace. The drop-tube furnace is a laboratory-scale furnace system that can simulate conditions in commercial combustors without the high cost associated with pilot-scale combustion testing. Figure 1 shows the drop-tube furnace used at the EERC. The combustion temperature, residence time, and gas cooling rate can be closely controlled and monitored (9).

Fly ash was collected using a Southern Research Institute Five-Stage Cyclone, equipped with a final filter, and a University of Washington Mark 5 Source Test Cascade Impactor. The multicyclone aerodynamically separates the fly ash into six stages or aerodynamic categories, while the impactor segregates the ash into twelve stages.

A short residence time probe was used to collect char samples at five residence time intervals: 0.05, 0.1, 0.2, 0.5, and 0.8 seconds. Particle-size distributions of original coal minerals and char phases were determined using CCSEM, and fly ash was sized using multicyclone and impactor collection devices attached to the drop-tube furnace. The effects of combustion temperature and coal particle size on the final fly ash size distribution were investigated as well.

Fly ash was produced at 1300, 1400, and 1500°C using 53-74 μm fractions of Beulah and Upper Freeport coals. The combustion parameters are given in Table 2. Near 100% carbon burnout was achieved under these conditions. The fly ash was cooled by means of a fly ash quenching probe and collected using the multicyclone. In addition, three size fractions of each coal were combusted at 1500°C and collected in the impactor to note changes in fly ash particle-size distribution with varying coal size (Table 3). Table 4 gives the combustion parameters used to produce chars from Upper Freeport and Beulah (53-74 μm) coals, respectively, at various residence times. Based on thermal gravimetric analysis, a steady decrease in carbon content was noted with increasing residence time for both coals, and by 0.8 seconds, near 100% burnout was achieved. The chars were analyzed using CCSEM to determine the size and composition of inorganic ash particles.

RESULTS AND DISCUSSION

Fly Ash Particle-Size Evolution

Detailed analysis was made of the Beulah and Upper Freeport inorganic components associated with the coal, char, and fly ash by observing area, weight, and number percent concentrations of inorganic components in different size categories. Number percent data refers to the number of particles in a particular size category, whereas weight percent data is a weighted average of the ash in different size categories which approximate a mass distribution. In effect, this gives a time-resolved look at the development of fly ash particle size which is helpful input into models which attempt to predict fly ash size and composition.

The analysis of Beulah char phases revealed that greater quantities of larger-sized particles were formed during char formation as compared to the original mineral size distribution (Figure 2). This may be evidence for coalescence of smaller inorganic particles to form larger ones.

The particle-size distribution for mineral phases in the Upper Freeport chars (Figure 3) shows an initial increase in the number of particles in the smaller size categories. By 0.8 seconds, however, larger quantities of phases are found in the >11.0 μm fraction than in the coal. This trend may indicate that, initially, fragmentation of mineral grains may be occurring with subsequent coalescence of ash particles as time in the hot zone progresses. Another trend noted for these coals is that the Upper Freeport, which had an overall larger mineral particle-size distribution than did the Beulah (Figure 4a), also produced a larger fly ash size distribution (Figure 4b). This may help answer the question as to whether the fly ash size distribution is heavily dependent on the size of the original discrete mineral phases.

The degree of coalescence in Beulah and Upper Freeport was examined by comparing the measured ash particle size-distributions with particle-size distributions at the extremes for total coalescence or no coalescence. The hypothesis is that the true fly ash size distribution should fall somewhere between ideal coalescence, where one ash particle is produced per coal particle, and no coalescence where each coal mineral grain remains intact as a separate particle. The predicted mean diameter (D_a) of an ash particle was derived using the ash % of the coal and the diameter (D_c) of the coal grains from Malvern (Equation 1). Assumptions made were that the coal particles were spheres

$$D_a = D_c \sqrt[3]{\%Ash} \qquad (1)$$

and that percent ash was evenly distributed throughout all the coal particles. The discrete minerals and the fly ash were sized using CCSEM. The size distribution curve for Beulah 0.8 second char, which closely approximates fly ash, falls between the mineral and predicted ash curves (Figure 5a). This is an indication of partial coalescence. Upper Freeport ash, on the other hand, follows very closely to the original coal size distribution for particles greater than approximately 3 microns (Figure 5b).

Both the Beulah and Upper Freeport showed some evidence of smaller fly ash particle size distributions at higher temperatures (Figure 6 a and b). Although the overall fly ash particle size was partially the result of coalescing mineral and organically bound constituents, early combustion stage char fragmentation may have occurred at higher temperatures resulting in finer-sized fly ash. To check the validity of smaller fly ash at higher temperatures, the number of fly ash grains produced per coal grain (F/C) was calculated for the fly ash size fractions in each multicyclone (Equation 2). The input variables needed to make the calculations were the mass of ash (m_n) in each multicyclone stage (n), total mass collected in the multicyclones (m_{tot}), density of the coal and ash (ρ_c and ρ_f), percent ash in the coal, and the diameters of the coal and fly ash grains (d_c and d_f). For simplicity, it was assumed that the coal and fly ash grains were spherical and had uniform densities of 1.4 and 2.7, respectively. Mean coal particle sizes (d_c) were obtained from Malvern sizing analysis, and the mean fly ash sizes (d_f) were calculated from the percent mass in each of the multicyclones. The same calculations apply for impactor data. The results

$$F/C = \frac{m_n \rho_c}{m_{tot} \rho_f} \left(\frac{\%Ash}{100}\right) \left(\frac{d_c}{d_f}\right)^3 \qquad (2)$$

of the calculations, given in Table 5a, are reported for fly ash grains greater than 1 μm. These very basic calculations verify the PSD data from the multicyclones that larger quantities of smaller fly ash particles are generated at higher temperatures. This may indicate that larger coal particles are reverting to the smaller-sized ash distributions dictated by the original coal mineral sizes as carbon matrix burns away.

Fly ash produced at 1500°C, using different Beulah coal size fractions and collected in the impactor, was larger for the smaller-sized coal fractions (Figure 7a). A similar result was achieved for Upper Freeport coal size fractions, especially for ash particles greater than 2.8 microns (Figure 7b). Calculations of fly ash particles generated per coal particle for the different coal size fractions showed more fly ash grains for the larger coal fractions, for both Beulah and Upper Freeport (Table 5b). Smaller minerals were observed earlier to experience a greater degree of coalescence. It may be that the smaller coal size fractions contain more smaller-sized minerals more apt to coalesce to form a larger ash particle.

CONCLUSIONS

Particle-size distributions of discrete mineral or amorphous phases in intermediates produced in the DTF for two coals were examined. Coal minerals and char inorganic phases approximately <3.0μm in the Beulah and Upper Freeport tend to coalesce with time. Upon combustion, the Upper Freeport shows an initial increase in the amount of particles in the lower size ranges, possibly due to fragmentation of minerals or the formation of smaller inorganic ash droplets from submicron minerals or inorganics. The Upper Freeport coal minerals PSD and resulting fly ash PSD are distributed over larger size ranges than the same PSDs for the Beulah.

The size distribution curve for Beulah ash falls between the mineral and predicted coalescence ash curves. This is an indication of partial coalescence.

Upper Freeport ash, on the other hand, follows very closely to the original coal size distribution for particles greater than approximately 3 microns. The mechanism may not necessarily be fragmentation of coal particles, but rather that as carbon matrix burns away, larger coal particles are reverting to the smaller-sized ash distributions as dictated by the original coal mineral sizes. Beulah, on the other hand, shows more coalescence influence, possibly due to the Na-Ca-rich phases from the organic bonding sites that envelop and react with aluminosilicates, resulting during combustion.

Particle-size distributions of the fly ash at three different temperatures showed slightly smaller fly ash sizes at the higher temperature for both coals. In support of this observation, both coals produced more fly ash particles per coal particle for higher combustion temperatures. Although the fly ash overall was a result of coalescing mineral and organically bound constituents, the early stage chars may have experienced more initial fragmentation at higher temperatures. Fly ash produced at 1500°C, using different coal size fractions and collected in the impactor, was larger for the smaller sized coal fraction.

The trends in fly ash formation observed here using empirical data are in agreement with various models of fly ash evolution and provide a good framework for verifying and testing future models.

ACKNOWLEDGEMENTS

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TABLE 1

INORGANIC CHARACTERIZATION OF BEULAH AND UPPER FREEPORT COALS

Coal Ash Analysis	Beulah	Upper Freeport
SiO_2	21.5	50.5
Al_2O_3	13.5	24.2
Fe_2O_3	10.8	12.8
TiO_2	1.0	1.3
P_2O_5	0.9	0.1
CaO	16.1	3.1
MgO	4.0	1.5
Na_2O	6.2	0.0
K_2O	0.2	3.7
SO_3	25.7	2.7
% Ash (Dry Basis)	6.9	19.6
CCSEM Mineral Analysis		
Quartz	17.5	12.6
Iron Oxide	1.6	1.9
Aluminosilicate	40.8	24.3
Ca-aluminosilicate	0.2	0.6
Fe-aluminosilicate	0.1	3.6
K-aluminosilicate	0.9	31.6
Pyrite	27.5	13.8
Gypsum	1.6	0.5
Barite	0.9	0.0
Calcite	0.1	1.1
Rutile	0.3	0.9
Pyrrhotite	0.7	1.3
Si-Rich	0.4	0.3
Unknown	6.7	6.9
Total Minerals (Coal Basis)	4.8	22.1

TABLE 2

DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION OF FLY ASH FOR BEULAH AND UPPER FREEPORT 53-74 μm COALS

	UPPER FREEPORT			BEULAH		
Run #	1	2	3	1	2	3
Gas Flow Rates (L\min):						
Primary air	1	1	1	1	1	1
Secondary air	4	4	4	3	3	3
Quench Gas (N_2)	4	4	4	3	3	3
Vacuum	10	10	10	10	10	10
Temperatures (°C):						
Secondary air	1000	1000	1000	933	930	930
Furnace Upper Wall	1298	1406	1498	1300	1400	1500
Furnace Lower Wall	--	1429	--	--	--	--
Coal Feed Rate (g/min)	0.13	0.09	0.06	0.29	0.45	0.31
Residence Time (sec)	2.5	2.4	2.3	2.5	2.4	2.3

TABLE 3

DROP-TUBE FURNACE RUN CONDITIONS FOR THE FORMATION OF FLY ASH FROM BEULAH AND UPPER FREEPORT COAL SIZE FRACTIONS

Coal Size, μm	38-53	53-74	74-106
Gas Flow Rates (L\min):			
Primary air	1	1	1
Secondary air	3-4	3-4	3-4
Quench Gas (N_2)	3-4	3-4	3-4
Vacuum	10	10	10
Temperatures (°C):			
Secondary air	980	990	980
Furnace 1 Upper Wall	1498	1500	1500
Furnace 1 Lower Wall	1530	1530	1510
Coal Feed Rate (g/min)	0.03-0.24	0.03-0.2	0.03-0.2
Residence Time (sec)	2.5	2.3	2.0

TABLE 4

DROP-TUBE FURNACE RUN CONDITIONS FOR CHAR COLLECTION
OF BEULAH AND UPPER FREEPORT 53-74 μm COALS

	Beulah				Upper Freeport				
Run #	1	2	3	4	1	2	3	4	5
Gas Flow Rates (L\min):									
Primary air	1	1	1	1	1.2	1.2	1.2	2	1.2
Secondary air	4	4	4	4	3	3	3	2.5	3
Quench Gas (N_2)	3	3	3	3	5	5	5	5	5
Vacuum	10	10	10	10	10	10	10	10	10
Temperatures (°C):									
Secondary air	1000	1000	1000	1000	982	982	983	982	992
Furnace 1 Upper Wall	1467	1470	1475	1442	1502	1498	1497	1503	1499
Furnace 1 Lower Wall	1487	1480	1478	1434	1572	1570	1563	1552	1545
Coal Feed Rate (g/min)	0.08	0.08	0.29	0.34	0.06	0.06	0.06	0.05	0.06
Residence Time (sec)	0.1	0.2	0.5	0.8	0.05	0.1	0.2	0.5	0.8

TABLE 5

CALCULATED FLY ASH GRAINS PER COAL GRAIN
(PARTICLES > 1 MICRON)

(a) Varied Temperature and 53-75 μm Coal

	Temperature °C		
	1300	1400	1500
Beulah	6.3	5.9	9.0
Upper Freeport	16.5	21.6	26.3

(b) Varied Coal Size

	Coal Size (μm)		
	38-53	53-74	74-106
Beulah	14	66	147
Upper Freeport	159	134	316

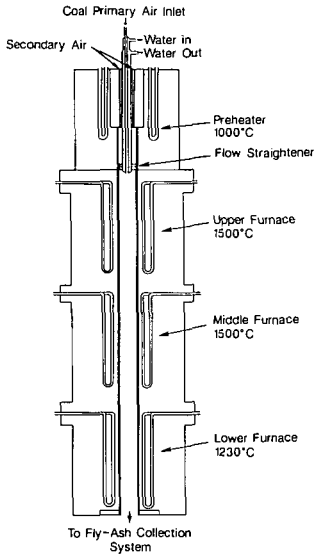


Figure 1. Schematic drawing of the EERC drop-tube furnace.

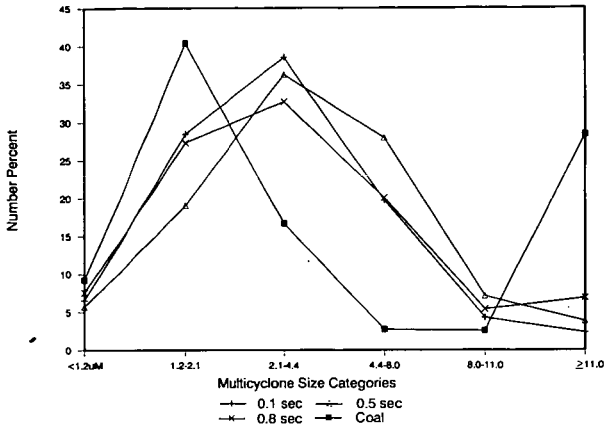


Figure 2. Particle-size distribution of inorganic particles in Beulah chars based on the numbers of particles in each size category determined using CCSEM of whole grain mounts.

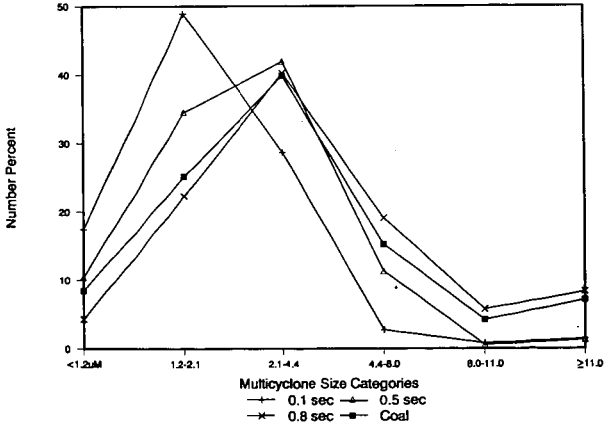
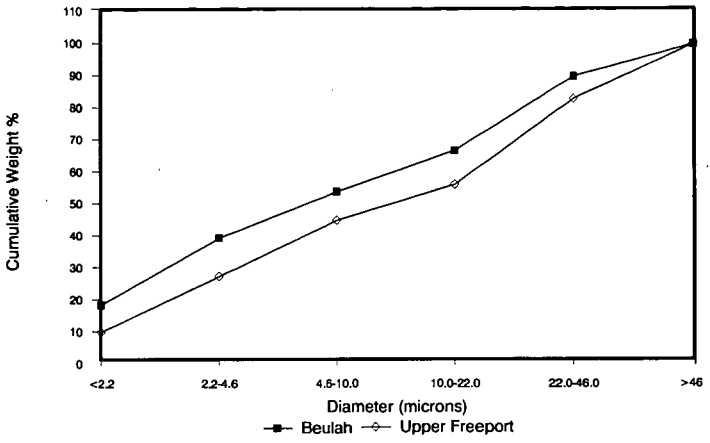


Figure 3. Particle-size distribution of inorganic particles in Upper Freeport chars based on the number of particles in each size category determined using CCSEM of whole grain mounts.

(a)



(b)

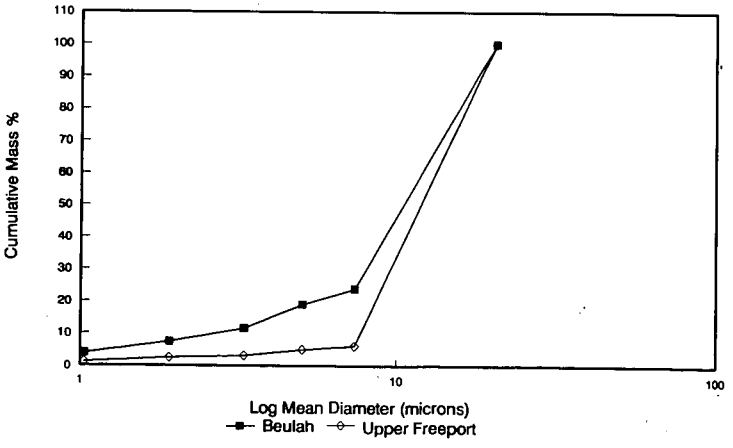


Figure 4. (a) Size distribution of minerals in Beulah and Upper Freeport 53-75 μm.
(b) Size distribution of fly ash in Beulah and Upper Freeport generated at 1500°C on the 53-74 μm fraction.

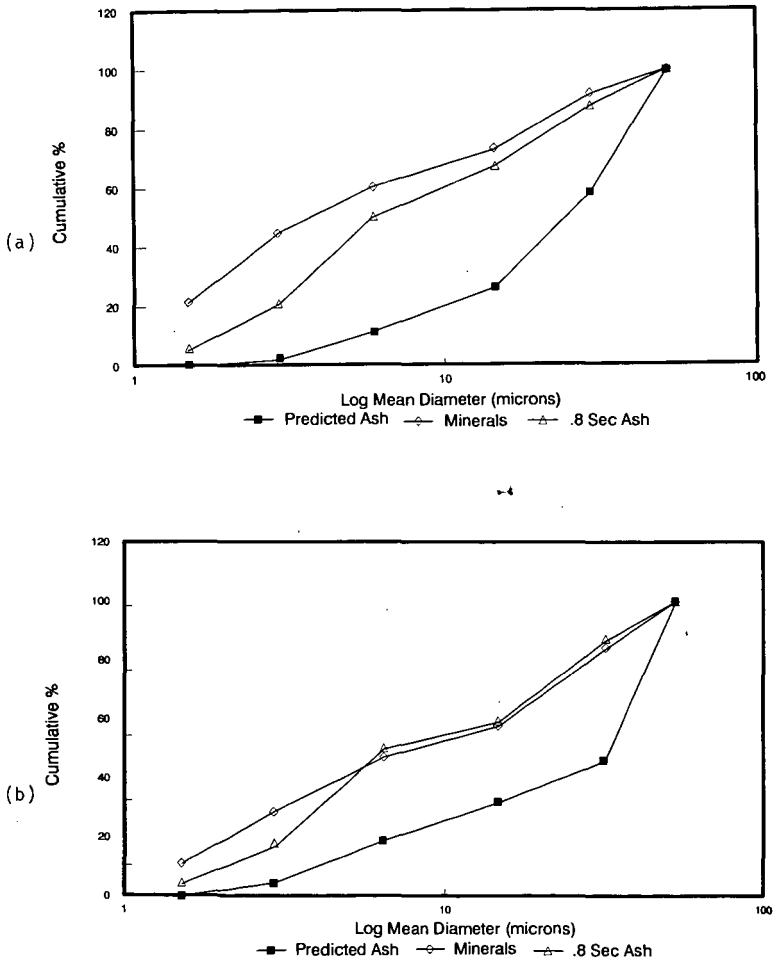
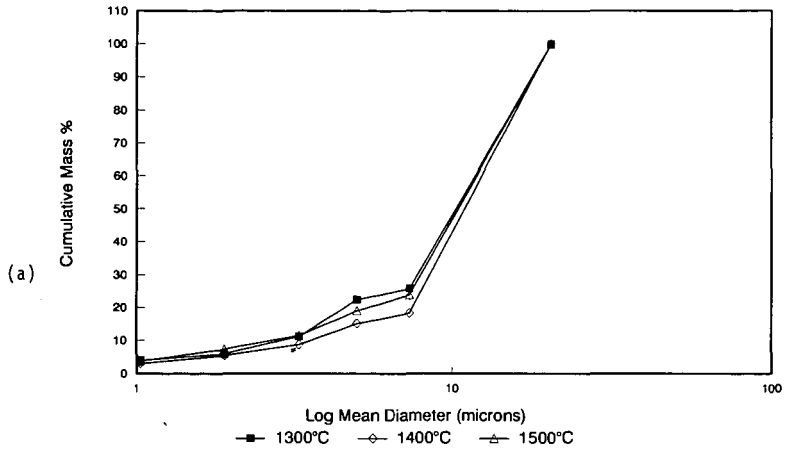


Figure 5. Cumulative particle-size distribution of predicted ash from total inorganic coalescence of each coal particle, coal minerals, and 0.8 fly ash, using CCSEM and Malvern data, for (a) Beulah and (b) Upper Freeport.



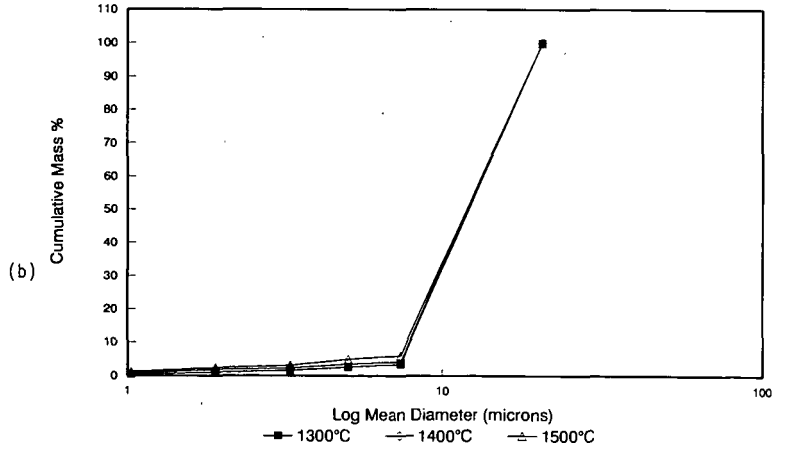


Figure 6. Fly ash particle-size distributions observed at 1300, 1400, and 1500°C after combustion of (a) Beulah and (b) Upper Freeport 53-74 μm coals.

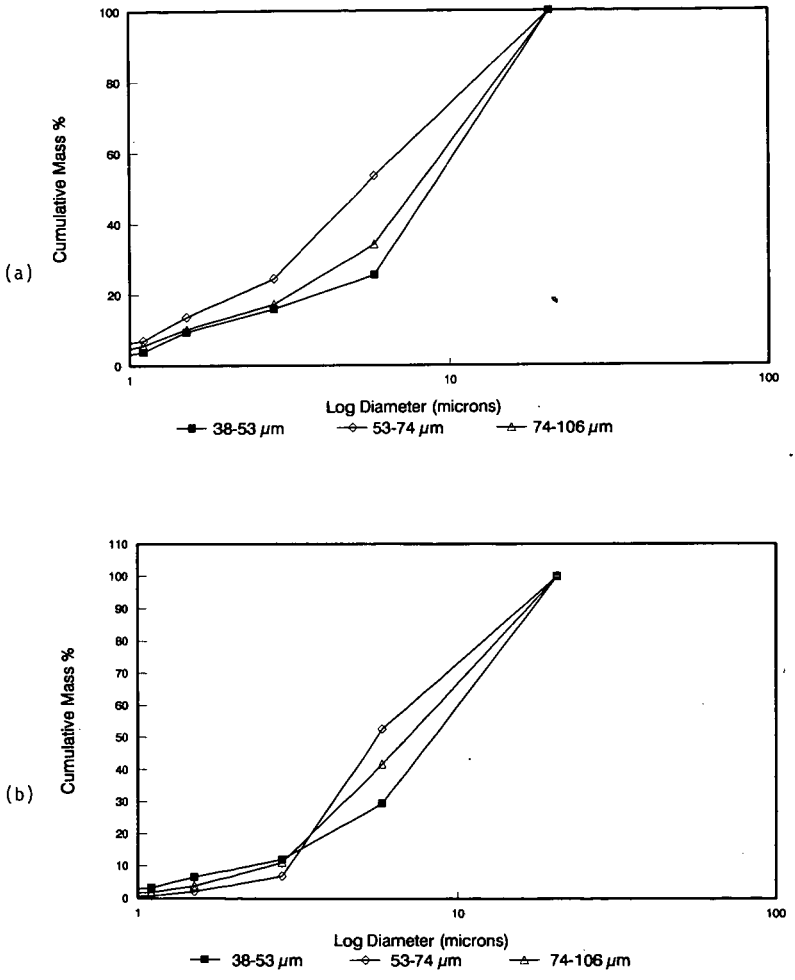


Figure 7. Fly ash particle-size distribution observed after combustion of 38-53, 53-74, and 74-106 μm coal size fractions of (a) Beulah and (b) Upper Freeport.